

# PATENT SPECIFICATION

(11) 1200414

1200414

## NO DRAWINGS

- (21) Application No. 1993/68 (22) Filed 12 Jan. 1968
- (31) Convention Application No. 608724 (32) Filed 12 Jan. 1967 in
- (33) United States of America (US)
- (45) Complete Specification published 29 July 1970
- (51) International Classification C 08 f 25/00
- (52) Index at acceptance

C3G 1B2 1C2 2B 2C 3A2 3C4



## (54) PRODUCTION OF GRAFT POLYMERS

(71) We, MONSANTO COMPANY, a Corporation organised under the laws of the State of Delaware, United States of America, of 800 North Lindbergh Boulevard, St. Louis, 66, State of Missouri, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of graft polymers.

It is known that polyblends of rubbers with monoethylenically unsaturated aromatic hydrocarbon polymers have significant advantages in providing materials having properties including toughness, processability and chemical resistance. Various processes have been suggested or used for the manufacture thereof including emulsion, suspension and mass polymerisation techniques.

The emulsion polymerisation techniques have been widely used and have enabled previously prepared aqueous latices of the diene polymer to be used as the reaction medium. It has also been suggested that the ratio of the graft superstrate to the rubber substrate may be varied over a wide range with consequent modification in the properties of the product. However, efforts to provide a high superstrate to substrate ratio have often encountered difficulties and have frequently resulted in graft copolymers having undesirably unbalanced properties. Mere increase in the amount of polymerisable monomers added to a rubber latex does not ensure the desired increase in the superstrate to substrate ratio in the product or the development of desirable properties. Moreover, the particle size of the graft copolymer is important for obtaining the desired balance of properties in a highly grafted rubber blend.

It is an object of the invention to provide an improved process for producing a graft polymer of a rubber with a monoethylenically unsaturated aromatic hydrocarbon poly-

mer which has a relatively high superstrate to substrate ratio and a desirable balance of properties.

According to the present invention there is provided a process for producing a graft polymer which comprises (1) polymerising to at least 60% by weight conversion an aqueous emulsion containing at least one conjugated diene monomer alone or in admixture with not more than an equal weight of one or more monoethylenically unsaturated monomers, a water-soluble free-radical forming polymerisation catalyst therefor and such an amount of emulsifying agent as will produce and maintain particles having a number average diameter of substantially 0.06 to 0.20 micron in the disperse phase of the emulsion and (2) introducing into the resulting diene polymer latex at least one polymerisable monoethylenically unsaturated aromatic hydrocarbon or halohydrocarbon monomer alone or together with at least one copolymerisable monomer, a molecular weight regulator and a water-soluble free-radical forming polymerisation catalyst therefor, the rate of introduction of the monomer or monomers into the latex being such as to ensure that the amount of unpolymerised monomer or monomers present therein does not exceed 10% of the weight of the diene polymer during the graft polymerisation of the first 50% of the monomer or monomers being introduced and does not exceed 20% of the same weight during polymerisation of the second 50% of the monomer or monomers being introduced, the total amount of monomer added being 80 to 300% by weight of the diene polymer whilst the amount of catalyst present in the polymerising mixture during introduction of the first 50% of monomer or monomers is in excess of that required for polymerisation of the monomer or monomers introduced and the introduction of any emulsifying agent other than that used in the production of the diene polymer latex is deferred until at least 30% of the monomer or monomers has or have been added to the latex so as to produce a polymer comprising

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a graft copolymer having a superstrate to substrate ratio of 50 to 150:100 by weight.

In carrying out the process of the present invention an aqueous emulsion containing a polymerisable diene monomer formulation, a water-soluble free-radical forming polymerisation catalyst and an emulsifying agent is first prepared. This emulsion is subjected to polymerisation conditions for a period of time sufficient to polymerise the diene monomer formulation to at least 60% by weight conversion while controlling the total content of emulsifying agent during the polymerisation cycle so as to produce and maintain latex particles having a diameter of about 0.06 to 0.20 micron.

After polymerisation of the diene monomer to the desired degree of conversion, there is admixed with the latex of the diene polymer a polymerisable monoethylenically unsaturated aromatic hydrocarbon or halo-hydrocarbon monomer formulation, a water-soluble free radical-forming polymerisation catalyst therefor and a molecular weight regulator. The monomer is added to the latex at such a rate as to provide in the admixture not more than about 10% by weight, based upon the weight of the diene polymer, of unreacted monomer formulation at any time during the addition of the first 50% by weight of the monomer formulation, this will take at least four hours. Similarly, the rate of addition is controlled during the addition of the second 50% by weight of the monomer so as to provide in the admixture not more than about 20% by weight of unreacted monomer on the same basis. The total amount of monomer formulation added to the latex is 80 to 300% by weight of the diene polymer.

The water-soluble free radical-forming polymerisation catalyst is added to the latex in an amount and at rates sufficient to provide an excess of catalyst over that required to polymerise the monomer introduced during the period of addition of at least the first 50% by weight of the monomer formulation and to provide sufficient catalyst for the polymerisation of the monomer formulation throughout substantially the entire polymerisation reaction. Since any significant excess of catalyst which will produce a residue of catalyst in the polymer is undesirable because of its effect upon the properties of the polymer the total amount of catalyst required to polymerise the monomer formulation substantially to completion is initially determined. Normally, the initial addition of the whole of the catalyst is not desirable. It is desirable to add to the latex only 20 to 50%, preferably 20 to 30%, of the total amount of catalyst either initially or during the addition of the first amounts of monomer. Additional catalyst is then added during the

addition of the monomer formulation to ensure that the proportion of catalyst added is at least 10% greater, preferably at least 15% greater, than the proportion of monomer formulation added during at least the addition of the first 50% of the monomer formulation. For example, 25% of the catalyst may be added to the latex before the addition of any monomer formulation, and increments of 10 to 15% added during the addition of each 10 to 15% by weight of monomer formulation, so that at least 65% of the catalyst has been added by the time 50% of the monomer formulation has been added.

It is imperative that there be an excess of catalyst during the initial half of the monomer addition to promote the grafting reaction.

The addition of additional emulsifying agent during the graft polymerisation reaction can create new rubber particles and so should be avoided during the addition of at least the first 30% of the monomer formulation, and preferably the first 50% thereof. The only additional emulsifier that may be required will be to maintain stability of the latex, and the amount should be limited to avoid deleterious effects upon particle size. In this manner, the graft reaction will result in a latex with graft particles having a diameter of about 0.06 to 0.20 micron. The admixture is subjected to polymerisation conditions to polymerise the monomer formulation and produce grafting of at least a portion thereof upon the diene polymer to provide a graft copolymer having a superstrate to substrate ratio of 50 to 150:100 by weight.

The diene monomer formulations used contain one or more conjugated 1,3-dienes such as butadiene, isoprene, piperylene or chloroprene. They may include not more than an equal amount by weight of one or more copolymerisable monoethylenically unsaturated monomers such as monoethylenically unsaturated aromatic hydrocarbons (e.g. styrene; an aralkylstyrene, such as the ortho-, meta- and para-methylstyrenes, 2,4-dimethylstyrene, the ar -ethylstyrenes and para-tertiary-butylstyrene); an alpha-alkylstyrene, such as alpha-methylstyrene, alpha-ethylstyrene or alpha-methyl-para-methylstyrene; a vinyl naphthalene; nuclear halogenated monoethylenically unsaturated aromatic hydrocarbons (e.g., the crtho-, meta- and para-chlorostyrenes, 2,4-dibromostyrene and 2 - methyl - 4 - chlorostyrene); acrylonitrile; methacrylonitrile, the alkyl acrylates (e.g. methyl, butyl and 2-ethylhexyl acrylates), the corresponding alkyl methacrylates, the acrylamides (e.g. acrylamide, methacrylamide and N-butylacrylamide); monoethylenically unsaturated ketones (e.g., vinyl methyl ketone and methyl isopropanol ketone); alpha-olefins

(e.g., ethylene and propylene); vinyl pyridines; vinyl esters (e.g. vinyl acetate and vinyl stearate); and the vinyl and vinylidene halides (e.g., the vinyl and vinylidene chlorides and bromides).

The diene monomer formulation may contain up to about 1.0% by weight of a cross linking agent to produce a desirable degree of cross linking in the rubber. However, excessive cross linking should be avoided since it can result in loss of the rubbery characteristics.

The cross linking agent may be any one of the agents conventionally employed for cross linking diene rubbers, including divinyl benzene, diallyl maleate, diallyl fumarate, diallyl adipate, allyl acrylate, allyl methacrylate and the diacrylates and dimethylacrylates of polyhydric alcohols, e.g., ethylene glycol dimethylacrylate.

A preferred group of rubbers are those consisting essentially of 75.0 to 100.0% by weight of butadiene and/or isoprene and up to 25.0% by weight of a monomer which is a monoethylenically unsaturated aromatic hydrocarbon (e.g., styrene) or an ethylenically unsaturated nitrile (e.g., acrylonitrile), or mixtures thereof.

Particularly advantageous substrates are butadiene homopolymer and interpolymers containing 90.0 to 95.0% by weight of butadiene and 5.0 to 10.0% by weight of acrylonitrile or styrene.

The polymerisable formulations to be grafted upon the diene rubber particles in the latex may vary in composition dependent upon the nature of the rubber substrate and the ultimate properties desired in the graft copolymer. In all instances, they include one or more monoethylenically unsaturated aromatic hydrocarbon or halohydrocarbon monomers either alone or together with a copolymerisable monomer or monomers.

The specific monomers will vary with the product desired. However, the process is advantageously used for the manufacture of styrene-type polyblends; i.e., polymerisable monomer formulations containing monoethylenically unsaturated aromatic hydrocarbons or halohydrocarbons either alone or together with other copolymerisable monomers such as monoethylenically unsaturated nitriles. Where a styrene-type monomer is employed alone, then the resultant product will be of the type known as an "impact styrene". Where styrene and acrylonitrile-type monomers are employed together, the resulting product will be of the type known as "ABS". However, it should be understood that the composition of the polymerisable formulation may vary widely.

Exemplary of the monoethylenically unsaturated aromatic hydrocarbon and halohydrocarbon monomers that may be homo-

polymerised or interpolymerised are styrene; the alpha-alkyl monoethylenically unsaturated monocyclic aromatic compounds, e.g., alpha-methylstyrene, alpha - ethylstyrene, alpha-methylvinyltoluene and alpha-methyldialkylstyrenes; the nuclear substituted alkylstyrenes, e.g. vinyl toluene, ortho-ethylstyrene, para-ethylstyrene and 2,4-dimethylstyrene; the nuclear substituted halostyrenes, e.g. ortho-chlorostyrene, para-chlorostyrene, ortho-bromostyrene and 2,4-dichlorostyrene; the nuclear alkyl, and halogen substituted styrenes, e.g., 2-chloro-4-methylstyrene and also vinyl naphthalene and vinyl anthracene. The alkyl substituents usually have one to four carbon atoms and may include isopropyl and isobutyl groups. If desired, mixtures of such monoethylenically unsaturated aromatic monomers may be employed.

Other ethylenically unsaturated monomers that may be interpolymerised with the monoethylenically unsaturated aromatic hydrocarbon and halohydrocarbon monomers are ethylenically unsaturated nitriles, such as acrylonitrile, methacrylonitrile, ethacrylonitrile and mixtures thereof; conjugated 1,3-dienes, e.g., butadiene and isoprene;  $\alpha,\beta$ -ethylenically unsaturated monobasic acids and functional derivatives thereof, e.g., acrylic acid, methyl, ethyl, butyl and 2-ethylhexyl acrylates, methacrylic acid and the corresponding esters thereof, acrylamide and methacrylamide; vinyl halides such as vinyl chloride and bromide; vinylidene chloride and bromide; vinyl esters such as vinyl acetate and propionate; dialkyl maleates and fumarates such as dimethyl, diethyl and dibutyl maleates and the corresponding fumarates. The amount of these comonomers which may be included in an interpolymer will vary.

The preferred polymerisable monomer formulations contain at least 10.0% by weight of monoethylenically unsaturated aromatic hydrocarbon or halohydrocarbon monomer and preferably at least 50.0% by weight thereof. Desirably, they contain an ethylenically unsaturated nitrile which should be present in the amount of at least 5.0%, and preferably at least 10.0% by weight thereof. From the standpoint of highly advantageous ABS-type products, the monomer formulations contain 20.0 to 95.0%, preferably 60.0 to 85.0% by weight of the monoethylenically unsaturated aromatic hydrocarbon such as styrene, and 80.0 to 5.0%, preferably 40.0 to 15.0%, by weight of the ethylenically unsaturated nitrile each as acrylonitrile.

To produce the desired emulsion of the diene monomer, emulsifying agents are employed in relatively small amounts depending upon the effectiveness of the emulsifying agent since the size of the dispersed phase is to be controlled as will be pointed out in

- more detail hereinafter. Suitable emulsifying agents are fatty acid soaps of alkali metals, alkali metal and ammonium soaps of high molecular weight, alkyl and alkaryl sulphates and sulphonates and mineral acid salts of long chain aliphatic amines. Dispersing aids and salts may also be included to effect the desired emulsification. Sodium oleate, palmitate and stearate, as well as other sodium soaps have been found particularly advantageous both alone and together with each other and with other emulsifiers and aids. 65
- The emulsifying agent is preferably used during the polymerisation of the diene monomers in an amount less than about 4.0% by weight based upon the diene monomer. The amount of the emulsifying agent present at any time should not be excessive so as to decrease the size of the dispersed particle below about 0.06 micron but should suffice to prevent formation of wall scale and agglomeration or increase in size of the particles to above 0.20 micron in diameter. The emulsifying agent added during polymerisation of the diene monomer is sufficient for emulsification of at least the first 30% of the monoethylenically unsaturated aromatic hydrocarbon or halohydrocarbon monomer formulation. However, in order to obtain latex stability and greater control over the emulsion and the particle size, small amounts of emulsifying agent may then be added during the remainder of the graft polymerisation reaction. Such additions should not deleteriously affect the particle size of the dispersed phase. 70
- The catalysts used both for the diene monomer polymerisation and graft polymerisation are the various water-soluble free radical generating polymerisation initiators conventionally used, including peroxy and azo catalysts. If desired, the same catalyst may be used for both the polymerisation reactions. Suitable peroxy catalysts are the alkali metal peroxides, persulphates, perborates, peracetates and percarbonates and hydrogen peroxide. If so desired, the catalysts may be activated to form redox systems. The amount of catalyst should be sufficient to effect polymerisation to the desired degree of both the diene monomer and the monoethylenically unsaturated aromatic hydrocarbon or halohydrocarbon monomer formulation. The amount of catalyst added will be dependent upon the activity thereof but must be closely controlled in the graft polymerisation reaction as will be more fully pointed out hereinbefore. 75
- A molecular weight regulator is preferably present during the diene monomer polymerisation and is used during the monoethylenically unsaturated aromatic hydrocarbon or halohydrocarbon monomer polymerisation reactions so as to control the molecular weight and achieve the desired properties. Suitable molecular weight regulators are the higher alkyl mercaptans and terpenes, specifically N-dodecyl mercaptan, tertiary dodecyl mercaptan, terpinolene and d-limonene. 80
- In addition, antioxidants and stabilisers may be incorporated in one or both of the polymerising formulations to prevent degradation such as the conventional alkylated phenols. If so desired, other substances such as pigments and fillers may be incorporated. 85
- The amount of water in which the polymerisable diene formulation is emulsified may vary depending upon the emulsifying agent, the polymerisation conditions and the particular monomer formulation. However, it should be appreciated that the ratio of monomer to water will tend to affect the size of the dispersed particles. Generally, the ratio by weight of water to monomer when using alkali metal soaps as dispersing agents will fall within the range of 80 to 150:100, preferably 90 to 125:100. 90
- The amount of emulsifying agent added should not be excessive so as to produce undue minimisation of the size of the dispersed particles of monomer and of the resulting polymer. However, too little emulsifying agent can lead to latex instability or large particle size or undue decrease in the rate of polymerisation. Since it is desired to control the size of the latex particles to substantially within the range of 0.06 to 0.20 micron, the effective amount of dispersing agent can be readily determined by observation in simple laboratory tests. In using alkali metal soaps as the primary or sole emulsifying agent, it has been found that the initial addition of 0.8 to 2.0 parts by weight of soap per 100 parts of the monomer formulation will generally be satisfactory. During polymerisation, it will usually be necessary to add additional emulsifying agent to maintain the stability of the latex and to control the particle size within the desired range. The total amount of alkali metal soap added should be less than 4.0 parts by weight per 100 parts of the diene monomer formulation, and preferably less than 3.5 parts. Accordingly, it has been found advantageous to limit the additional soap to two charges of 0.5 to 1.5 parts. 95
- The catalyst concentration will determine the rate of polymerisation and the ultimate degree of conversion to a large extent. Similarly, the particular catalyst will determine the amount thereof required to achieve the desired rate of reaction. The amount of catalyst is desirably kept below 1.0%, and preferably below 0.5% by weight of the monomer. The preferred catalysts are peroxy catalysts. 100
- In addition, the emulsion may contain various salts which reduce the micelle con-

centration in the aqueous phase, or which depress the viscosity. Dispersing aids which prevent agglomeration of the latex particles are also advantageously included. In order to control the molecular weight of the rubber, it is desirable to include in the formulation molecular weight regulators, such as the mercaptans, the amounts thereof being limited so as to avoid undue effect upon the rate of polymerisation.

The rubber polymerisation reaction may be carried out under a variety of conditions depending upon the catalyst system and the desired polymerisation cycle. A particularly advantageous process is one using a peroxy catalyst and a reaction temperature of 50 to 70°C with but autogenous pressures. In such a process, it is possible to effect more than 90% conversion of the diene monomer formulation within times of ten to twenty hours.

After polymerisation of the diene monomer formulation to the desired degree of conversion, unreacted diene monomer is desirably removed to avoid any deleterious effect upon the grafting reaction. By polymerising to substantially complete conversion, this problem may be minimised. The resulting latex should have particles having a diameter of substantially 0.06 to 0.20 micron, preferably about 0.08 to 0.15 micron.

To the thus produced latex are now added the several components for carrying out the graft polymerisation process. The emulsifying agent already in the latex should be sufficient for emulsification of at least the first 30% of the new monomer formulation and other components.

The polymerisable monomer formulation is added to the latex in relatively small amounts, and preferably continuously, so as to ensure that the amount of unpolymerised monomer formulation will not exceed 10.0% by weight of the diene polymer at any time during the graft polymerisation of the first 50% of the monomer formulation: this may be expected to require at least four hours. Preferably, the amount is less than 5.0% by weight. The rate of addition of the monomer formulation is also controlled during the addition of the second half so that the content of unreacted monomer formulation at any time is below about 20%, preferably less than 10%, by weight of the diene rubber. By controlling the amount of unreacted monomer present at any time, and particularly during the initial graft polymerisation, it has been found that the grafting of the monomer formulation upon the rubber can be promoted.

However, the catalyst concentration must also be controlled so as to achieve the desired promotion of grafting over polymerisation of matrix particles. Since it is imperative that the grafting reaction is encouraged, an excess of catalyst over that required to polymerize the monomer present should be

available during the addition of the first 50%, preferably during the addition of the first 65%, by weight of the monomer formulation. After 65% of the monomers have been added, the catalyst concentration should be sufficient to maintain the desired polymerisation reaction and produce polymerisation of at least 90%, preferably at least 98%, by weight of the total monomer formulation.

A molecular weight regulator is desirably incorporated in the latex to control the molecular weight of the resulting polymer to within the range of 15,000 to 100,000 and preferably 25,000 to 45,000 (number average molecular weights based upon gel permeation chromatography or osmometry), to obtain optimum flow characteristics in the resulting polymer. Since the monomer formulation is being added over an extended period of time, the molecular weight regulator should also be added in small amounts during substantially the entire period of such addition so as to avoid any undue effect upon the molecular weight or upon the polymerisation reaction. Desirably, the molecular weight regulator is admixed with the polymerisable monomer formulation so as to be added therewith in the desired proportion. The amount of molecular weight regulator will vary with the molecular weight regulator selected but will usually be from 0.5 to 2.0% by weight of the polymerisable monoethylenically unsaturated aromatic hydrocarbon or halohydrocarbon monomer.

Small amounts of emulsifying agent may be added after the graft polymerisation reaction has proceeded to at least 30%. In some instances, the addition of 0.5 to 1.0% by weight, based upon the weight of the rubber, of an emulsifying agent has been beneficial at about 35 to 90% conversion of the monomer formulation.

The particular polymerisation conditions employed will vary with the monomer formulation and with the catalyst. The rate of reaction will increase with increase in temperature, although a limiting factor is possible deterioration in properties of the product and also decrease in the graft ratio, as well as instability of the latex. Temperatures of 50 to 100°C and pressures of 0 to 35 p.s.i.g. have been found suitable for a fairly efficient graft polymerisation reaction. An inert atmosphere may be employed over the polymerising latex.

After the polymerisation reaction has proceeded to the desired degree of conversion of the monomer formulation, any unreacted monomers may be removed if so desired, the latex coagulated and the polyblend washed and recovered. The amount of matrix will, of course, vary with the efficiency of the graft reaction and the ratio of monomer formulation to rubber which has been

charged. Accordingly, it may be desirable to blend additional monoethylenically unsaturated aromatic hydrocarbon polymer with the polyblend produced by this process to obtain the desired formulation.

The graft copolymer in the polyblend will be found to have a particle size in the range of 0.06 to 0.20 micron, preferably 0.08 to 0.15 micron, as determined by number averaging in electron microscope evaluation. The graft ratio of superstrate to substrate will be found to be from 50 to 150:100, preferably 75 to 125:100 by weight. The polyblends thus produced are found to have desirable shrinkage characteristics, high gloss and a satisfactory level of impact strength, as well as a desirable balance of other properties.

The following example wherein all parts are parts by weight unless otherwise indicated, illustrates the nature of the invention.

#### EXAMPLE

To a suitable reactor are charged 93.0 parts of butadiene, 7.0 parts of acrylonitrile, 0.3 part of potassium persulphate, 1.25 parts of a dispersing aid (a condensation product of a naphthalene sulphonic acid and aldehyde sold as "Darvan"), 2.0 parts of tetrasodium pyrophosphate, 0.4 part of dodecyl mercaptans and 1.25 parts of a rubber reserve soap. The water content is adjusted to provide a solids content of 45%. The resulting aqueous mixture is agitated to produce a substantially homogeneous emulsion which is swept out with nitrogen and then subjected to polymerisation conditions to convert more than 95% of the monomers. During the polymerisation cycle, the temperature varies from 50 to 70°C, and the pressure from 45 to 120 p.s.i.g. An addition of 2.0 parts of rubber reserve soap is made three hours after commencement of the cycle. Upon completion of the polymerisation, the unreacted monomers are vented to the atmosphere, and the latex particle size is found to be about 0.11 micron (number average).

To the rubber latex thus formed are added 1.1 parts of potassium persulphate and 350 parts of water. A mixture is made of 3.0 parts of terpinolene and a polymerisable monomer formulation containing 140.0 parts of styrene and 60.0 parts of acrylonitrile. The reactor is swept out with nitrogen gas and then subjected to polymerisation conditions while the mixture of the monomer formulation is continuously added thereto over a period of six hours.

During the polymerisation cycle, the temperature is maintained at 65 to 80°C and the pressure at 0 to 15 p.s.i.g., the total cycle being approximately eight hours. An addition of 0.5 parts of rubber reserve soap is made to the polymerising mixture at 5.33 hours after the start of the cycle. Additional

persulphate catalyst (1.7 parts) is added between 1.5 and 6 hours after commencement of the polymerisation cycle.

The reactor is then vented and antioxidants and stabilisers are added. The latex is next coagulated, washed and dried to provide a blend containing graft copolymer with a superstrate to substrate ratio of about 75:100 and a particle size (number average) of 0.13 micron. This blend is then moulded to provide suitable specimens for testing. The moulded specimens are found to have the following properties:

Gloss, Hunter Peak	100	65
Shrinkage, Per Cent	6.0	70
Lacquerability*	Excellent	75
Flow, cm.**	2-5	80
Izod Impact, foot pounds/inch notch 73° F. 1/2"×1/4"	0.8	85
Falling Dart Impact Strength at 0°F., foot pounds (100 mils Thickness)	1.0	90

\*In the lacquerability test, trapezoidal injection moulded specimens measuring 3 inches at the top, 5 inches at the bottom, 3 inches in height and 0.1 inch thick are sprayed with lacquer on both sides and allowed to dry. The surface opposite the knock-out pins is studied for evidence of crazing and the area of crazing is estimated.

\*\*This test measures the relative flow of various blends by use of a 3-ounce Fellows injection moulding machine with a standard die having a cavity 150 mils in thickness, one inch in width and 30 centimetres in length. The machine conditions are standardised at 450°F. stock temperature, 140°F die temperature, and a pressure of 1000 pounds. Fifty cycles are run and the length of the specimens from the last thirty specimens is averaged to determine the amount of filling of the cavity which will measure the flowability of the polymer.

Thus, it can be seen that the graft polymers produced in accordance with the present invention provide excellent gloss, shrinkage and lacquerability. In addition, they have been found to exhibit highly advantageous tensile properties while retaining some degree of impact strength. With such compositions, it is possible to obtain excellent properties from the standpoint of appearance whilst retaining a measure of mechanical properties sufficient to enable application of the product for various purposes where appearance is of primary importance.

Moreover, by blending the graft polymers produced in accordance with the present invention with other graft copolymers having a lesser degree of grafting even in very low amounts, compositions having relatively high impact strengths with highly desirable appearance may be obtained.

**WHAT WE CLAIM IS:—**

1. A process for producing a graft polymer which comprises (1) polymerising to at least 60% by weight conversion an aqueous emulsion containing at least one conjugated diene monomer alone or in admixture with not more than an equal weight of one or more monoethylenically unsaturated monomers, a water-soluble free-radical forming polymerisation catalyst therefor and such an amount of emulsifying agent as will produce and maintain particles having a number average diameter of substantially 0.06 to 0.20 micron in the disperse phase of the emulsion and (2) introducing into the resulting diene polymer latex at least one polymerisable monoethylenically unsaturated aromatic hydrocarbons or halohydrocarbon monomer alone or together with at least one copolymerisable monomer, a molecular weight regulator and a water-soluble free-radical forming polymerisation catalyst therefor, the rate of introduction of the monomer or monomers in to the latex being such as to ensure that the amount of unpolymerised monomer or monomers present therein does not exceed 10% of the weight of the diene polymer during the graft polymerisation of the first 50% of the monomer or monomers being introduced and does not exceed 20% of the same weight during polymerisation of the second 50% of the monomer or monomers being introduced, the total amount of monomer added being 80 to 300% by weight of the diene polymer whilst the amount of catalyst present in the polymerising mixture during introduction of the first 50% of the monomer or monomers is in excess of that required for polymerisation of the monomer or monomers introduced, and the introduction of any emulsifying agent other than that used in the production of the diene polymer latex is deferred until at least 30% of the monomer or monomers has or have been added to the latex so as to produce a polymer comprising a graft polymer having a superstrate to substrate ratio of 50 to 150:100 by weight.
2. A process as claimed in claim 1 in which any conjugated diene monomer remaining at the end of the first stage of the process is removed prior to carrying out the grafting reaction.
3. A process as claimed in claim 1 or claim 2 in which any emulsifying agent introduced during the graft polymerisation is only added after the first 50% of the monomer or monomers has or have been added to the latex.
4. A process as claimed in any of the preceding claims in which the diene polymer latex is produced by polymerising 75—100% by weight of butadiene and/or isoprene and up to 25% by weight of a monoethylenically unsaturated aromatic hydrocarbon or an ethylenically unsaturated nitrile.
5. A process as claimed in claim 4 in which the diene polymer latex is produced by polymerising butadiene alone or 90—95% by weight of butadiene and 5—10% of styrene or acrylonitrile.
6. A process as claimed in any of the preceding claims in which there is introduced into the diene polymer latex a monomer mixture comprising 60—85% by weight of monoethylenically unsaturated aromatic hydrocarbon monomer and 40—15% by weight of an ethylenically unsaturated nitrile.
7. A process according to any of the preceding claims in which the rate of introduction of the monoethylenically unsaturated aromatic hydrocarbon monomer and any copolymerisable monomer is such that the amount of unpolymerised monomer or monomers present in less than 5% of the weight of the diene polymer during addition of the first 50% of the monomer or monomers.
8. A process according to any of the preceding claims in which the rate of introduction of the monoethylenically unsaturated aromatic hydrocarbon monomer and any copolymerisable monomer is such that the amount of unpolymerised monomer or monomers present is less than 10% of the weight of the diene polymer during addition of the second 50% of the monomer or monomers.
9. A process according to any of the preceding claims in which the amount of catalyst present in the polymerising mixture containing monoethylenically unsaturated aromatic hydrocarbon monomer and any copolymerisable monomer is in excess of that required for polymerisation of the monomer or monomers present during introduction of the first 65% thereof.
10. A process according to any of the preceding claims in which molecular weight regulator is introduced into the diene polymer latex over substantially the same period as introduction of monoethylenically unsaturated aromatic hydrocarbon monomer.
11. A process for producing a graft polymer according to claim 1 and substantially as hereinbefore described with reference to the Example.
12. Graft polymers whenever produced by the process of any of the preceding claims.

**STEVENS, LANGNER, PARRY &  
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Chartered Patent Agents,  
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